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QUEEN MARY COLL LONDON (ENGLAND) DEPT OF CHEMISTRY F/G 7/4
KINETIC STUDIES INVOLVING ELECTRONICALLY-EXCITED INTERHALOGENS --ETC(U)
JAN 80 M A CLYNE AFOSR-75-2843

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
<p>The following areas are covered: (a) kinetics of chemiluminescent reactions involving excited B states of halogens and interhalogens; (b) measurement of halogen atom concentrations; (c) studies of halogens and interhalogens by laser-induced fluorescence. Citations to 26 papers are given.</p>			

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SUMMARY OF WORK

Kinetic Studies Involving Electronically-Excited Interhalogens and Halogens

1. Senior Research Personnel: Dr. I. S. McDermid; Dr. J. P. Liddy; Dr. E. Martinez; Professor S. Toby; Professor S. Jaffe; Dr. D. J. Smith.
2. Junior Research Personnel: Mr. P. D. Whitefield; Mr. M. C. Heaven.
3. Abstract of Objectives and Accomplishments

(a) Kinetics of chemiluminescent reactions involving excited B states of halogens and interhalogens.

The kinetics of the chemiluminescent atom-recombination reactions $\text{Cl} + \text{Br} + \text{M} \rightarrow \text{BrCl}(\text{B}) + \text{M}$, $\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2(\text{B}) + \text{M}$ and $\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M}$ have been determined. Branching ratios for forming the excited states were determined; all lie in the range 0.01 to 0.1.

The kinetics of the chemiluminescent reaction of Br_2 with OClO have been studied. The overall reaction was characterized as a branched-chain process. The branching ratio for forming excited $\text{BrCl}(\text{B})$ is > 0.05 .

New spectroscopic data on the B and X states of BrCl are reported.

(b) Measurement of halogen atom concentrations

Methods based on atomic resonance absorption and fluorescence have been developed for measuring Br and $\text{Cl}^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ atom concentrations over a wide range of densities, and in mixtures of different halogen atoms. The variation of oscillator strength within the $(n+1)s - np^5$ resonance multiplets has been exploited in wavelength-resolved atomic resonance studies.

(c) Studies of halogens and interhalogens by laser-induced fluorescence (LIF)

A state-of-the-art narrow-band, pulsed dye laser has been used to study the quantum-resolved dynamics of excited $\text{B}^3\Pi(0^+)$ states of Cl_2 , Br_2 , BrCl , BrF , IF , ICl and IBr and the $\text{A}^3\Pi(1_u)$ state of Br_2 . The first observation of quantum-resolved LIF is described for all of these molecules other than $\text{Br}_2(\text{B})$. The first direct determinations of radiative lifetimes by LIF is described for the B states of Cl_2 , BrF , Br_2 , IF and for the A state of Br_2 . Detailed studies of predissociation dynamics are reported. Measurements of rate constants for electronic quenching, collisional predissociation and ro-vibrational transfer are reported. In most cases, quenching of the B states is slow, but vibrational transfer is fast, thus favouring the B-X transitions as electronic-transition laser candidates.

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